

CARBON-14-CONTAINING COMPOUNDS PRODUCED BY  
THE PILE-NEUTRON IRRADIATION OF CYANOGUANIDINE

by

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## INTRODUCTION

In a flux of thermal neutrons, nitrogen atoms undergo the nuclear transformation  $N^{14}(n,p)C^{14}$ . In normal pile-neutron irradiations, the compound to be irradiated is also subjected to gamma radiation. Both the gamma radiation and the nuclear reactions initiated by the neutrons are capable of supplying energy to promote chemical reactions which normally would occur only at elevated temperatures.

Collins and Calkins(6) have estimated the average energy of the gamma rays in the Oak Ridge graphite reactor to be approximately 1 Mev. Few nuclear reactions are initiated by the absorption of gamma rays at this photon energy and thus, the important nuclear reactions are those produced by the neutrons.

The cyanoguanidine molecule is interesting for studying the chemical consequences produced by the nuclear transformation  $N^{14}(n,p)C^{14}$  for two reasons:

- (1) Within the cyanoguanidine molecule, the nitrogen atoms are bound to carbon atoms by three different types of bonding: single, double and triple bonds. With this compound, one might also study the effects of bonding upon the final chemical species containing the recoil carbon-14 atom.
- (2) The presence of the four nitrogen atoms within the cyanoguanidine molecule permits the production of an adequate specific activity within a reasonable irradiation period.

Naturally occurring nitrogen is 99.635 per cent nitrogen-14 and 0.365 per cent nitrogen-15(29). The thermal neutron cross section for nitrogen-14

is 1.70 barns(17). The carbon-14 half life of 5760 years, reported by Mann, et. al.(26), has been used for calculations in this study.

The carbon-14, produced from nitrogen by the (n,p) reaction, recoils with an average energy of about 42,000 ev. The average recoil energy,  $\bar{E}_M$ , of the product atom when one particle of mass,  $m$ , is emitted from the compound nucleus is given by(42)

$$\bar{E}_M = (E_1 + Q)(m/M) + E_1(m_1/M) \quad (1)$$

where  $E_1$  is the energy of the incident particle,  $Q$  is the energy released in the nuclear reaction,  $m_1$  is the mass of the incident particle and  $M$  is the mass of the compound nucleus. The calculations made using the above equation are valid only when the mass of the recoil particle is much greater than the mass of the incident particle. With  $Q$  equal to an average value of 0.628 Mev(1, 7, 8),  $m$  equal to the mass of a proton and  $M$  equal to the mass of the compound nucleus; the average recoil energy,  $\bar{E}_M$ , is calculated to be approximately 42,000 ev. The 42,000 ev recoil energy of carbon-14 is sufficient to break one or more chemical bonds present in the cyanoguanidine molecule. For example, the carbon-nitrogen triple bond is the strongest bond between the two elements and has an energy of 8.4 ev(13).

Immediately after acquiring this energy, the recoil atom moves through the adjacent surroundings at a high velocity. This energy is dissipated by collisions with other molecules and when the energy of the recoil atom is sufficiently reduced it may enter into chemical recombinations or other reactions.

### Theoretical Considerations

Various theories have been advanced in attempts to explain the processes occurring during the period immediately after the recoil atom has broken all its bonds and becomes mobile, to the point of incorporation of the recoil atom into some ultimate chemical specie.

Two of the theories advanced were proposed to rationalise the yields observed in the condensed phase in  $(n,\gamma)$  studies of alkyl halides; however, they have been extended to other systems as well. These two theories are the "billiard ball collision-epithermal collision" theory, proposed by Libby(20, 21) and the "random fragmentation", or "nest of radicals" theory, proposed by Willard(45).

The billiard ball-collision theory, advanced by Libby(20), postulates that the recoil atoms in the liquid or solid medium lose their energy by momentum transfer in elastic collisions with single atoms. This assumes that the transfer occurs in the same manner as if the atoms were isolated atoms in the gaseous phase. A head-on collision of the recoiling atom with another atom, of approximately the same mass, would result in nearly a 50 per cent energy transfer to the struck atom, thus projecting it into the medium. These atoms, in turn, transfer energy to other atoms or molecules within the medium to melt a pear-shaped region in the solid with a volume of the order of  $10^3$  molecules. The recoil atom would remain in the solvent cage with the radical produced as a result of the collision and so would have a high probability of combining with the radical to form a stable chemical species. If the recoil atom had struck the atom at a different angle, a glancing collision rather than a head-on collision would have occurred and the energy transfer

would not have been as complete. In this case, the recoil atom might escape from the solvent cage without undergoing recombination with the radical produced.

A head-on collision of the carbon-14 recoil atom with a hydrogen atom would have resulted in the loss of about 25 per cent of the energy of the recoil atom and the recoil atom would retain nearly 75 per cent of the energy previous to the collision. Therefore, the recoil atom would not be expected to stay in the solvent cage with the radical formed by the bond breakage.

The billiard ball theory predicts that all of the recoil atoms would enter combination such that the parent compound is re-formed. The results of numerous investigations have shown that the final chemical state of the recoil atom is not entirely that of the parent compound. Libby(21) suggested that this might be explained by assuming that when the energy of the recoil atom was reduced to approximately 10 ev by successive collisions with other atoms, a new type of energy transfer would become possible. In the range of  $E < 10$  ev, but not in the higher energy regions, the recoil atom may transfer energy to molecules as a whole by inelastic collisions, with the subsequent breakage of one of the bonds of the molecule resulting from vibrational excitation. If, for example, a hydrogen bond were ruptured in an inelastic collision, the recoil atom would remain in the solvent cage with the radical formed and thus would have a high probability to substitute for the hydrogen atom in forming a stable chemical specie. These types of reactions have been termed "epithermal" in contrast to those occurring at the higher energies.

Willard(45) postulated the "random fragmentation" theory, in which,

the recoil atom in a liquid or solid phase acquires a recoil energy of several hundred electron volts and starts to move rapidly through the medium. When the recoil atom has traveled less than a molecular diameter, it encounters a solvent molecule. If this were an isolated molecule, as in Libby's theory, the energetic recoil atom would transfer part of its energy to the molecule or to one of its atoms and continue through the medium. In the liquid or solid phase, this cannot happen since the struck molecule is surrounded by a closely packed and sometimes intertwined wall of other solvent molecules. The result is that the energy is dissipated by an indiscriminate rupture of bonds in the immediate vicinity of the energetic recoil atom. When the energy of the recoil atom has been reduced below the energy required to rupture bonds, the carbon-14 recoil atom will be located in, or adjacent to, a pocket containing a high concentration of radicals and atoms. The recoil atom may combine with one of the radicals after the energy of the recoil atom has been reduced where combination is possible, but before it has had an opportunity to diffuse into the medium as a thermal atom. An alternate mechanism is that it may enter stable combination by a thermal process, after diffusion in thermal equilibrium with the medium. In systems where the activation energy for the various reactions of the recoil atom with the solvent is high, the thermal atom nearly always combines with a radical or ion which it produced during the dissipation of its recoil energy. These radicals or ions are encountered by the recoil carbon-14 atom after collisions with the solvent molecules.

The relative number and the specific types of fragments formed by the recoil atom depends on the chemical nature, structure, and density of the medium and on the mass and energy of the recoil atom. It may also depend upon

the activation energies for its reactions with the other molecules of the medium.

Recently Harbottle and Sutin(14) have applied the "displacement spike" concept, proposed by Seitz and Koshler(36), to construct a model for nuclear transformations in solids, and to consider how the recoil atom disposes of its high energy and the various processes in returning it to stable chemical combination.

The "displacement spike" theory distinguishes between two energy regions.

(1) The hot region in which all reactions occur before the recoil atom reaches thermal equilibrium with its environment. This region includes all energies above 0.025 ev; (2) The thermal regions in which the recoil atom is able to diffuse through the environment and undergo the more familiar chemical reactions as recombination, exchange, addition and substitution.

Reactions occurring in the hot region may be of two general types: (a) reactions proceeding by the direct replacement of an atom within a molecule by the recoil atom; (2) chemical reactions similar to those which occur in the thermal region but which are modified by the local higher temperatures.

Immediately after the formation of the recoil atom, the atom may lose energy by electronic excitation or by ionization during the slowing-down process. For recoil energies less than 20 kev, in all cases of chemical interest, the recoil atom will not lose electrons or ionize the surrounding atoms. In some cases, the recoil atom may be positively charged at the beginning of the path. However, at the end of its travels, it will be in that oxidation state in which the removal of an electron from the lattice requires more energy than that possessed by the recoil atom. It is also necessary to consider the environment



of the recoil atom in addition to the various energies possessed by the recoil atom during the slowing-down process. The binding forces in ionic crystals are stronger than those in molecular crystals so that environmental factors in ionic crystals will be more important in determining the probability of electron transfer than in molecular crystals. The initial chemical state of the recoil atom is also of importance in considering the probability of electron transfer. In ionic crystals, if the recoiling atom is initially in a high chemical oxidation state, the probability of electron transfer to the medium will be less than if the atom had initially been in a lower oxidation state. In molecular crystals, where intramolecular bonding is predominately covalent, the recoil atom probably starts out, and remains to the end of its range, a neutral atom.

The primary atom, or recoil atom, dissipates approximately half of its energy by producing secondary atoms through displacement reactions and the remainder is lost in excitation of lattice vibrations. For typical recoil energies of approximately 300 ev, the recoiling atom produces about 6 atomic displacements in the slowing-down process in ionic crystals and, because of the weaker intermolecular binding, the recoil atom will produce about 16 atomic displacements in molecular crystals. Due to the higher recoil energy, the carbon-14 recoil atom would produce a larger number of atomic displacements. These ionic and molecular crystals normally contain several kinds of atoms of different masses and different oxidation states such that collisions between atoms of different masses must also be considered. The maximum energy which the recoil atom can transfer to an atom of different mass in a collision is given by

$$E_m = \frac{4 M_1 M_2}{(M_1 + M_2)^2} E_1 \quad (2)$$

where  $M_1$  and  $M_2$  are the mass of the recoiling and struck atoms, and  $E_1$  is the energy of the recoil atom before the collision. The recoil atom will undergo more collisions in the slowing-down process in a medium where its mass is different than that of the surrounding atoms since the maximum energy transfer in a collision occurs between two atoms of the same mass.

Reactions in which the recoil atom ejects a bound atom and takes its place have been termed "replacement or interchange collision" and are of considerable importance in chemical systems. A successful interchange collision can occur wherever the energy transferred to the struck atom by the recoil atom is greater than the energy required to displace the atom to an interstitial position and the energy of the recoil atom is decreased to less than that required to displace the struck atom within the same collision. Since the cage energy is higher in solids than in liquids, due to the stronger intermolecular forces and greater density, conditions are more favorable for a recombination reaction in solids than in liquids. Recombination reactions are more probably in ionic crystals than in molecular crystals for molecules of comparable complexity and bond strength.

If one assumes that only elastic collisions occur and the carbon-14 recoil atom loses on the average approximately seven-tenths of its energy in each elastic collision with an atom of the cyanoguanidine molecule, a relatively small number of collisions (approximately 7) will be required to reduce its energy below 10 ev, where the recoil atom may begin to become stable towards chemical recombination. The total time required for this slowing-down process is of the order of  $10^{-13}$  sec. and the mean free path

of the atom is about  $5r$ , where  $r$  is the atomic radius(14). This abrupt loss of most of the energy within a small volume will produce a very high local "temperature". These small volumes of high "temperature" are termed "hot-spots". The recoil atom is thermalized in a series of about 5 to 10 hot-spots which lie within a radius of about  $10r$ . These local hot-spots merge within a time of about  $10^{-12}$  sec. to form a hot zone or "displacement spike". The hot zone in an ionic crystal lattice involves a volume of the order of  $10^3$ - $10^4$  molecules and remains at a temperature above the melting point for approximately  $10^{-11}$  sec. Similar considerations indicate that an equal amount of energy dissipated in a molecular crystal lattice with a lower melting point, will melt a volume approximately four times as great as that for an ionic lattice. Due to the smaller thermal conductance in molecular solids, the hot zone will remain above the melting temperature for a longer period of time than that in an ionic crystal lattice. Since liquids are generally better thermal conductors than solids, the life-time of the "displacement spike" in solids will be longer than in liquids. The heat factor and the larger cage energies will increase the number of reactions in the hot zone when a compound is irradiated in the solid phase rather than in the liquid phase. In view of the high temperatures produced in the hot zone, additional fragments may exist due to the thermal dissociation of molecular crystals.

Within the hot zone, there is a good chance that the recoil fragments will react with one of the species in its immediate vicinity provided the energy of activation is not too high. The neighbors of the recoil fragments will be parent molecules, if a pure compound is irradiated. This favors the reaction of the recoil fragment with the parent species and the products corresponding to this reaction will be produced in addition to products resulting from the

recombination of the recoil fragment with a collision fragment.

#### Previous $N^{14}(n,p) C^{14}$ Studies

The first reported analysis for the chemical species containing the recoil carbon-14 atom, produced by thermal neutron irradiation of nitrogen-containing organic or inorganic compounds, was by Yankwich, Rollefson and Morris(58). Crystalline ammonium nitrate, urea, hydrazinium chloride and glycine were irradiated with thermal neutrons. Aqueous solutions of ammonium nitrate, urea, and pyridine and pure aniline were also subjected to irradiation with neutrons. Following the irradiation, the samples were dissolved in water and analyzed for various compounds, containing one carbon atom, such as carbon dioxide, methane, formaldehyde and methylamine. Carbon dioxide and carbon monoxide were found to contain over 90% of the total isolated activity in aqueous and crystalline ammonium nitrate samples. Hydrogen cyanide was observed to contain 55% and 71% of the total isolated carbon-14 activity in crystalline urea and hydrazinium chloride, respectively. Approximately 50% of the activity isolated from the irradiated crystalline glycine was present in the form of methanol. Inconclusive results were obtained from the irradiation of aqueous pyridine and pure aniline. Yankwich, et. al. concluded from their results that carbon dioxide and carbon monoxide are the predominate species containing the recoil carbon-14 atom in those compounds which contained oxygen within the molecule and that carbon dioxide tends to be formed in greater abundance than carbon monoxide. Methane- $C^{14}$  appeared only in the absence of oxygen in the molecule and in the presence of a high hydrogen density. Hydrogen cyanide, containing the recoil carbon-14, was found to occur only in the absence of a high oxygen concentration, while methanol and formic

acid tended to appear only in the presence of water.

Giacomello and Zifferero(11) irradiated crystalline ammonium oxalate with thermal neutrons and dissolved their sample in water before analyzing for the various chemical species containing the recoil carbon-14 atom. Approximately 11% of the total activity produced was found in oxalic acid, with smaller amounts in carbon monoxide, carbon dioxide and hydrogen cyanide. The chemical form of the remainder of the total activity produced, 77%, was not determined.

Yankwich(54) irradiated solid beryllium nitride with thermal neutrons and, upon dissolution of the sample in water, determined that 63% of the total activity produced was in the form of methane. Smaller amounts were present as carbon monoxide, carbon dioxide and hydrogen cyanide. An oxidisable fraction, primarily formic acid, was found to contain 27% of the total carbon-14 activity. Later, Yankwich and Cornman(57) irradiated solid beryllium nitride again and an analysis of the irradiated compound gave 26% of the induced total activity as methane. Guanidine, methylhydrazine and carbon dioxide were found to contain 19%, 11% and 14%, respectively, of the total activity produced during the neutron irradiation. The latter results differ quite significantly from those previously obtained. The difference between the two results was attributed primarily to an incomplete analysis of the former beryllium nitride sample. Yankwich and Cornman concluded that the appearance of nitrogenous compounds among the final products was evidence that the skeletons of complex chemical species are formed and remain stable in the irradiated crystals.

Barbieri, et. al.(2) subjected solid phenylalanine to thermal neutron irradiation. The solid was dissolved in water, following the irradiation.

These investigators analyzed for 23 different chemical species that may have contained the recoil carbon-14 atom. The separation of many of the products was accomplished by paper and column chromatographic techniques. Aspartic acid, formic acid and glutaric acid were found to contain 5%, 4% and 4%, respectively, of the total induced carbon-14 activity. The remainder of the isolated activity, was found in small amounts in the remaining compounds. The authors were unable to account for 64% of the total induced carbon-14 activity. The significance of the results obtained was not discussed since only about one-third of the activity was determined.

Yankvich and Vaughan(59) found that 80% of the activity produced by the neutron irradiation of solid ammonium bromide was present as methylamine. Following irradiation, the target sample was dissolved in water, and analyzed for the various chemical species. Small amounts of activity were also found in the form of methane, formaldehyde and carbon dioxide. The results were discussed in terms of matrix-stabilized species which, upon addition to water, interact with the solvent to produce chemically stable products. The high yield of methylamine was interpreted as evidence for the high stability of the C-H linkages within the matrix of the irradiated crystals.

Belluco, et. al.(3) studied the various chemical species produced by the neutron irradiation of solid ammonium nicotinate. Analysis of the irradiated compound, after dissolution in water, showed that 16% of the total carbon-14 activity was introduced into malonic acid, with lesser amounts of the activity in compounds such as nicotinic acid, butyric acid, benzoic acid, and carbon dioxide. They were able to account for only 32% of the total activity induced in the sample by the neutron irradiation.



Cacace and co-workers(4) subjected solid benzanilide to analysis for the various chemical species produced by the neutron irradiation of the solid sample. Upon dissolution of the target material in water, carbon monoxide was found to contain 12% of the total induced activity. Carbon dioxide, hydrogen cyanide and benzanilide were found to contain smaller amounts of activity, while methylamine, formaldehyde, formic acid and benzene were found to be essentially free of any induced activity. The total isolated activity accounted for only 22% of the total induced carbon-14 activity.

Zifferero(63) and Giacomello(10) independently studied the chemical species resulting from the irradiation of crystalline quinoline oxalate. In each study, naphthalene and oxalic acid were found to contain the greatest amount of activity with smaller amounts present in the form of quinoline,  $\alpha$ -naphthol and carbon dioxide. The isolated activity accounted for only approximately one-fifth of the total carbon-14 activity in each of the studies. Conclusions based on the results obtained in the studies were not presented. Giacomello(9) found that benzene contained 8% of the total induced activity obtained by irradiation of pyridine oxalate in the solid state. Phenol, carbon dioxide and carbon monoxide were found to contain lesser amounts of the induced activity. The isolated activity accounted for only 15% of the total induced activity in the solid target material.

Crystalline  $\text{Ni}(\text{CN})_2 \cdot \text{NH}_3 \cdot \text{C}_6\text{H}_6$  was irradiated with thermal neutrons by Zifferero(61). Analysis of the target material, after dissolution in water, showed activity present in the form of oxalic acid, benzene and hydrogen cyanide, with trace amounts present in carbon monoxide and carbon dioxide.

Yankwich and Cornman(56) determined the chemically isolatable species

resulting from the neutron irradiation of crystalline ammonium sulfate. Dissolution of the target material in water showed that 40 per cent of the total activity was in the form of carbon dioxide. Methylamine, formic acid and formaldehyde were isolated from the aqueous solution of the irradiated ammonium sulfate and were found to contain 16%, 16% and 13%, respectively, of the total activity produced in the sample. Lesser amounts of activity were present in hydrogen cyanide and urea. The results indicated that possibly many of the radiocarbon compounds were produced in the crystalline matrix and trapped in the matrix under strain of the solid. It was also suggested that the activity may possibly result from reactions with the solvent of carbon-containing species trapped in the crystalline lattice.

Crystalline hydrazine oxalate was irradiated with neutrons by Zifferero and Cieri(62). Analysis of the target material, dissolved in water, showed that formic acid, oxalic acid and methylamine contained 13%, 11% and 10%, respectively, of the total activity produced during the neutron irradiation. Lesser amounts of activity were present in carbon dioxide, formaldehyde and carbon monoxide. Crystalline naphthalene was added to the sample prior to irradiation in an effort to label the naphthalene by the recoiling carbon-14 atom. The results showed no measurable amounts of activity present in the naphthalene after irradiation. Analysis of the isolatable species resulting from the irradiation accounted for only 48% of the total induced activity. These results, together with some of the results mentioned previously, emphasize the fact that in the larger and more complex nitrogen-containing molecules not all of the induced activity is present in chemical species which can be readily isolated from the system.

The use of the recoil carbon-14 atom produced in the irradiation of



nitrogen-containing compounds have been investigated as a tool for the synthesis of compounds incorporating the recoil carbon atom. In these investigations, only the particular products of interest were isolated from the mixture.

The neutron irradiation of crystalline acetamide was carried out by Wolf, et. al.(50). Their approach centered on the re-entry product, acetamide, and the synthesis product, propionamide. Acidic and basic hydrolysis of the amides to the acids was carried out to determine the possible differences in state of the irradiated material. Analysis of the irradiated sample showed acetic acid contained 8% of the total activity while propionic acid contained 5% of the total induced activity. The results were discussed in terms of proposed mechanisms for the formation of the re-entry and synthesis product. Degradation studies were carried out on the products obtained by the irradiation and the activity present at each position was determined.

Zifferero(60) carried out the neutron irradiation on a series of crystalline organic oxalates. The target samples were analyzed to determine the activity present in oxalic acid and in the free organic base. The analysis showed oxalic acid to contain 2%, 1%, 1.5%, 3% and 4% of the total induced activity in the oxalates of pyridine, quinoline, isoquinoline, aniline and N-methylaniline, respectively. The free bases were found to contain 2%, 2%, 10%, 8% and 11%, respectively, of the total induced activity.

Wolf and co-workers(48, 49, 53) have irradiated a series of crystalline organic compounds and analyzed the target materials for the incorporation of the carbon-14 recoil atom in specific chemical species. Benzene and toluene, isolated from an irradiated sample of 2-methylpyrazine, containing a small amount of benzene, were found to contain 1.9% and 1.0%, respectively, of the

total induced activity. Acetic acid and propionic acid were isolated from an irradiated sample of acetamide by acidic and basic hydrolysis of the target material. The acetic acid was found to contain 6.5% of the total activity by basic hydrolysis and 8.1% of the activity by acidic hydrolysis. Propionic acid contained 6.7% and 5.0% of the total induced activity by basic and acidic hydrolysis, respectively. An analysis of irradiated acridine showed that 3.5% of the total induced activity was present in the parent compound and 0.2% of the total activity was present in naphthalene. Gases evolved from the sample were found to contain 3% of the total activity with the remaining activity present in the form of a polymeric material. Solid solutions of azobenzene and stilbene, containing varying amounts of azobenzene in the stilbene, were analysed for the activity present in the form of stilbene, azobenzene and benzalaniline. The results showed that as the mole fraction of azobenzene increased, the per cent of the total activity as azobenzene increased and the per cent as stilbene decreased. Measurable amounts of activity were found in benzalaniline at only 10 and 71.5 mole per cent azobenzene. The results also showed that by a comparison of the activities found in the benzene rings of the two components in the system, the ring activity yield of stilbene and azobenzene were nearly equal when comparing pure azobenzene to an extrapolated value for stilbene. The authors concluded that the ring entry is apparently not effected by the nature of the exocyclic structure.

Muxart(27) irradiated crystalline 5,6-benzacridine with neutrons and analysed the target material for the activity present in the form of 5,6-benzanthracene- $C^{14}$  and 5,6-benzacridine- $C^{14}$ . The analysis showed that 0.2% and 4.0% of the total induced activity was present as 5,6-benzanthracene and

5,6-benzacridine, respectively.

The irradiation of crystalline benzamide and benzenesulfonamide with thermal neutrons was carried out by Cacace, et. al.(5). The irradiated benzamide was analyzed for the activity incorporated in aniline, benzamide and benzoic acid. The analysis showed that 4.1%, 3.3% and less than 0.1% of the total induced activity was present in the isolated benzamide, aniline and benzoic acid, respectively. The irradiated benzenesulfonamide was analyzed for the activity present in phenol, benzamide and benzoic acid. The results of the analysis showed that 4.2%, 1.5% and 0.9%, respectively, of the total induced activity was present in the three samples. Mechanisms were given for the reactions leading to the final incorporation of the recoil carbon-14 atom in each of the isolated species.

Norris and Snell(30) investigated the large scale pile production of  $C^{14}$  by thermal neutron irradiation of aqueous solutions of ammonium nitrate. They found that the greatest majority of the  $C^{14}$  was liberated as carbon dioxide and carbon monoxide. The carbon dioxide- $C^{14}$  and carbon monoxide- $C^{14}$ , after conversion of the carbon monoxide to carbon dioxide, was precipitated as barium carbonate.

The labeling of organic molecules employing an external nitrogen-containing compound as the source of the recoil carbon-14 atom has been reported by several authors. Professor W. F. Libby has been the major contributor to these labeling studies and the majority of the results reported in the literature are due to his investigations.

Libby and MacKay(22, 23) irradiated solutions of *n*-pentane and isopentane

with thermal neutrons. Small amounts of aniline were added to each sample prior to irradiation to serve as the source of nitrogen. The chemical species produced by the neutron irradiation were separated from the solution by fractional distillation. Analysis of the low boiling hydrocarbons showed that *n*-hexane, 3-methylpentane and *n*-heptane contained 12%, 8% and 6%, respectively, of the total activity induced into the *n*-pentane sample. 3-methylpentane, 2-methylpentane and 2,2-dimethylbutane were found to contain 9%, 7% and 6%, respectively, of the total activity induced into the isopentane sample. The remainder of the activity isolated from the lower boiling hydrocarbons was found in many of the hydrocarbons from butane to hexane. The higher boiling hydrocarbons were analyzed by selecting two hydrocarbons which would produce a boiling range of from ten to sixty degrees. The activities isolated in these fractions were not analysed to determine the specific chemical species. A polymeric material was found to contain 26% and 28% of the total activity of *n*-pentane and isopentane, respectively.

Solutions of carbon tetrachloride, containing small amounts of aniline and pyridine, were irradiated with thermal neutrons by Hein, et. al.(15). Analysis of the irradiated samples showed that about 31 per cent of the total activity induced into the samples was found in the carbon tetrachloride.

Libby and Schrodtt(24) irradiated a series of nitrogen-containing compounds and nitrogen compounds dissolved in various solvents. In the analysis of irradiated aniline, 23% of the total induced activity was isolated in fourteen different chemical species resulting from the irradiation. The analysis of the irradiated 8% aniline in benzene sample showed that 62.5 per cent of the total activity remained in the benzene layer after acid extraction. Analysis

of the chemical species present in the benzene layer accounted for 9.5 per cent of the activity observed in the layer. Isolation of the chemical species resulting from the irradiation of 10% aniline in methanol accounted for essentially 100 per cent of the total induced activity. Methane, methanol and *n*-propanol contained 34%, 16% and 9%, respectively, of the total activity. The remainder of the activity was present in the higher alcohols and a basic fraction. The benzene layer resulting from the analysis of the irradiated triphenylamine contained 69 per cent of the total activity. The chemical species present in the benzene layer were not isolated. A sample of aniline hydrofluoride was irradiated with neutrons and the analysis of the target material showed that 32% of the total activity was extracted into 0.1 *N* hydrochloric acid layer. The chemical species present in the extract were not identified. Ethylamine, ethylamine hydrofluoride and methylamine hydrofluoride were also irradiated with neutrons. In the analysis of the target materials essentially 100 per cent of the total induced activity was isolated. Various amines were found to contain essentially all of the activity produced in each of the three samples.

Wolf and Yang(52) have conducted gas phase irradiations of pure anhydrous ammonia and ammonia-inert gas mixtures with thermal neutrons. Mixtures of ammonia with oxygen and methane and pure methylamine were also irradiated. Methane was found to contain 94% of the total induced activity in pure ammonia and over 90% of the total induced activity in the mixtures of ammonia with neon, xenon and oxygen. Analysis of the ammonia-methane mixture showed that 60% of the activity was present as methane and 34% of the activity as a polymer. The irradiation of pure methylamine produced 10-20 per cent of the total induced activity in a polymer. The chemical species containing the

remainder of the activity were not identified. The authors concluded from these results that a hydrogen transfer occurs during the limited but finite lifetime of an intermediate formed by an elastic collision between the carbon fragment and the hydrogen source.

Wolf(46) discussed the use of the recoiling carbon-14 atom as a technique for labeling organic compounds. The percentages of incorporation of the recoil carbon-14 are expressed as per cent of  $C^{14}$  found in the particular compound relative to the total amount of  $C^{14}$  produced during the irradiation. The chemical effects of the nuclear transformation  $^{14}N(n,p)^{14}C$  has been discussed in detail by Yankwich(55). Results obtained by Yankwich and co-workers are interpreted in terms of the Libby hard-sphere model and the Seitz-Koehler model. Comparisons between the distribution of the radiocarbon products and the oxidation state of the carbon atom is made.

Excellent review articles concerning the isotopic labeling of organic compounds through neutron irradiation and the chemical effects of the nuclear transformation have been given by Wolf(47) and Muxart(28).

## EXPERIMENTAL

The experimental procedure used to study the chemical changes produced in cyanoguanidine by thermal neutron irradiation will be discussed in the following order: preparation of the cyanoguanidine for irradiation; pile-neutron irradiation of the samples, and the chemical and radiochemical analysis of the irradiated cyanoguanidine.

### Sample Preparation

Cyanoguanidine, Eastman Red Label, was recrystallized twice from distilled water and dried in an electric oven at 100°C for one hour. 4.952 gm. of the dry, purified cyanoguanidine (M.P. = 205°C) was placed in a 8 cm x 2 cm diameter quartz ampoule. Prior to filling the ampoule with the purified compound, the quartz ampoule was treated with chromic acid, washed and dried thoroughly in an electric oven. After filling the ampoule with the purified cyanoguanidine, the ampoule and contents were attached to the vacuum line with a quartz 10/30 standard taper joint in a vertical position. Care was taken to remove all traces of oxygen and water vapor from the sample. This was accomplished by alternately evacuating and flushing the system several times with argon. After flushing the system several times with argon, the ampoule and contents were evacuated to a pressure below one micron; the quartz ampoules were then sealed off using a hand torch.

### Irradiation of the Cyanoguanidine Sample

Irradiation of the cyanoguanidine was carried out at Oak Ridge National Laboratories in the ORNL graphite reactor. At the location in the graphite reactor where the irradiation was made, the neutron flux was stated to be



approximately  $5 \times 10^{11} \text{ cm}^{-2} \text{ sec}^{-1}$ , with an accompanying gamma-ray flux of  $4.9 \times 10^5 \text{ r hr}^{-1}$ . The sample was irradiated for 28 days at the ambient pile temperature (less than  $80^\circ\text{C}$ .). Upon completion of the irradiation, the sample was returned to our laboratories. The sample was stored for 15 months before the ampoule was opened and the analyses made.

The amount of decomposition produced in the cyanoguanidine by the gamma-ray flux present during the pile-neutron irradiation was estimated in the following manner. One roentgen is equivalent to the absorption of approximately 100 ergs per gram of material. A G value of 4 is assumed, (40) where the term G value is the number of molecules decomposed by the absorption of 100 ev of energy. Since the gamma-ray flux was approximately  $5 \times 10^5 \text{ r hr}^{-1}$  for this irradiation, the energy absorbed by the sample is calculated to be  $5 \times 10^7 \text{ ergs/gm/hr}$ . The total irradiation time was approximately 670 hours and, thus, the total energy absorbed by the sample was  $3.4 \times 10^{10} \text{ ergs/gm}$ , or  $1.7 \times 10^{11} \text{ ergs}$  for the 5 gm sample. Converting ergs to electron volts, a value of  $1.1 \times 10^{23} \text{ ev}$  was obtained as the total energy absorbed by the sample. Multiplying the total energy absorbed the sample by the G value and the reciprocal of Avagadro's number, a decomposition of  $7 \times 10^{-3} \text{ moles}$  was obtained. Multiplication of the number of moles decomposed by the reciprocal of the number of moles of sample indicates that approximately 12% of the sample was damaged by the gamma-rays during the irradiation period, if the assumed value of  $-G(\text{cyanoguanidine}) = 4$  is valid.

The chemical effects produced by the rather extensive decomposition of the sample by the gamma-rays was not investigated in this study, since the primary interest was in the stable chemical species incorporating the recoil carbon-14 atom.



### Analysis of the Irradiated Sample

The quartz ampoule containing the irradiated cyanoguanidine was opened under vacuum by means of the apparatus shown in Figure 1. The ampoule was placed in the brass cylinder and the port to the cylinder was closed and sealed with Apieson-"W" to give a vacuum tight closure. The entire system was evacuated to a pressure of less than one micron and the stopcock was then closed off from the system. The brass cylinder was removed from the vacuum manifold and shaken until the ampoule was broken by impact on the projecting sharpened machine-screw. The cylinder was reconnected to the vacuum line and evacuated to the stopcock. The gases evolved upon breakage of the quartz ampoule were then allowed to expand into an auxiliary vacuum system and collected. The irradiated compound and pieces of the broken quartz ampoule were transferred, under an argon atmosphere, to a stoppered pyrex weighing bottle. The sample was maintained under an argon atmosphere during the entire course of the experimental study.

The total carbon-14 activity of the irradiated sample was determined by the dissolution of accurately weighed portions of the sample in distilled water using volumetric glassware. Aliquots were taken and the total activity determined using liquid scintillation counting techniques.

In order to establish the distribution of the carbon-14 activity among the species likely to result upon dissolution of the irradiated samples in water, the samples were dissolved in distilled water contained in an inverted Y-tube connected to the vacuum system; the solutions were then subjected to analyses for the various species present.

A small sample (50-100 mg) of the irradiated cyanoguanidine was placed

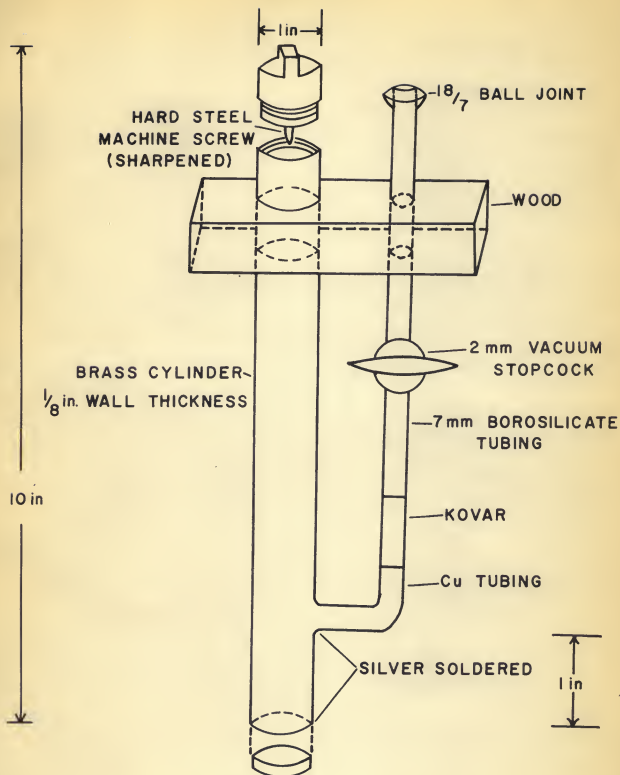


FIGURE 1 ILLUSTRATION OF SAMPLE OPENER

in one arm of the inverted Y-tube and distilled water (approximately 5-10 ml) was placed in the other arm. The Y-tube was connected to the vacuum line and the water degassed by alternately freezing with liquid air and warming while under vacuum. The auxiliary system was fitted with a cold trap, a 250 ml bulb for collecting the evolved gases and a mercury manometer. The entire system could be evacuated and closed off from the main manifold of the vacuum system. The Y-tube was closed off from the immediate system and the ice was allowed to melt. The water was added slowly in steps to the dry sample while alternately opening the Y-tube to the evacuated system. Upon addition of all of the water to the sample, the pressure change was recorded with the manometer and the collection bulb was closed off. The gaseous contents of the collection bulb were analyzed for carbon-14 containing chemical species evolved by dissolution of the sample in water.

#### Total Carbon-14 Activity

The total activity produced in the 4.952 gm sample of cyanoguanidine was determined to be  $18.6 \pm 0.7$  microcuries. This is an average value obtained from four different determinations on different samples made over a period of four months. The error quoted is one standard deviation.

#### Chemical Separations

The principle problem encountered in the analysis was the quantitative separation of the various activities free from contamination. Therefore, all components and derivatives isolated were purified to constant specific activity to achieve radiochemical purity.

Carbon Dioxide. Carbon dioxide was determined by direct adsorption on

sodium hydroxide or caroxite. The carbon dioxide evolved during the addition of water to the sample was removed by the insertion of a trap, containing either sodium hydroxide or caroxite (5-20 mesh), into the system between the Y-tube and the gas collection bulb. The sodium hydroxide or caroxite was subsequently dissolved in distilled water and a known aliquot removed to determine the radiocarbon activity.

Carbon Monoxide. Carbon monoxide evolved upon sample dissolution was subjected to gas chromatographic radioanalysis using Linde molecular sieve 5A as column packing. Radioanalyses were made by passing the effluent from the column directly through a proportional counter, after mixing with an argon-methane mixture.

Hydrogen Cyanide. Direct adsorption on sodium hydroxide was used to collect hydrogen cyanide, in a manner similar to that described above for carbon dioxide. The hydrogen cyanide was evolved by the addition of a 50% aqueous sulfuric acid solution to a sample of the cyanoguanidine contained in the Y-tube.

Methane. Gas chromatographic radioanalysis was also used for the methane evolved upon sample dissolution; the procedure was the same as that employed for carbon monoxide.

Formaldehyde. To an aliquot of a degassed solution of the irradiated sample containing carrier formaldehyde was added a solution of Methene (dimedon) in 95% ethanol. The solution was allowed to stand for 12 hours at room temperature. The precipitate formed was filtered, repeatedly recrystallized from a 50% ethanol-water mixture to a constant specific activity, and dried at 115°C for 20 minutes (16, 44). A weighed portion of the derivative

was dissolved directly in the scintillator solution and counted.

Formic Acid. Ten ml. of 1.0 M acetic acid and 50.0 ml of a solution, prepared by dissolving 100 gms of mercuric acetate in 1 liter of 0.5 M acetic acid, were added to an aliquot of the degassed sample after addition of carrier formic acid. The solution was brought to reflux, and the carbon dioxide evolved was swept into an absorption tower containing a 16% sodium hydroxide solution(35, 43). An aliquot of the sodium hydroxide solution was dissolved directly in the scintillator solution and counted.

Methylamine. An aliquot of an aqueous solution of the irradiated cyanoguanidine with carrier methylamine added was cooled in an ice bath for approximately 10 minutes. Phenylisothiocyanate was added and the solution shaken rapidly for 3-5 minutes.(\*) Precautions were taken to avoid adding an excess of the phenylisothiocyanate to the aqueous sample since an excess of the isothiocyanate produces a yellow oil which is very difficult to separate from the solid derivative. The precipitate was filtered, washed with a cold 50% aqueous ethanol solution and repeatedly recrystallized to a constant specific activity from 95% ethanol.(37) A weighed portion of the N,N'-Methylphenylthiourea was dissolved directly into the scintillator solution and its activity determined.

Urea. Jack bean urease was added to an aliquot of an aqueous solution of the irradiated sample containing carrier urea; this solution had been previously buffered to a pH of 6.8-7.0 with a phosphate buffer solution.(38) The solution was allowed to stand at room temperature for 12 hours and then

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(\*) Secondary amines, such as dimethylamine, also react to form the phenylthiourea derivatives.

was treated with an excess of dilute sulfuric acid. The carbon dioxide evolved was swept into an absorption tower containing a 16% sodium hydroxide solution.(59) A known volume of the sodium hydroxide solution was dissolved directly in the scintillator solution and counted.

Cyanoguanidine. Carrier cyanoguanidine was dissolved in an aliquot of an aqueous solution of the irradiated sample by warming. Care was taken to avoid heating the solution above 80°C, since cyanoguanidine decomposes slowly in water above this temperature, liberating ammonia. After cooling, the crystals were separated by filtration and recrystallized from distilled water to a constant specific activity. An aliquot of the cyanoguanidine was dissolved in water, added to the scintillator solution, and counted.

Guanidine. Cyanoguanidine was removed from an aliquot of an aqueous solution of the sample as described above. To the filtrate was added carrier guanidine and then a saturated solution of oxalic acid; guanidine oxalate separated from the solution as white crystals after the addition of ethanol to the aqueous solution. The precipitate was filtered and recrystallized from an ethanol-water mixture to a constant specific activity. The precipitate was dissolved in hydrochloric acid and the solution was then added directly to the scintillator solution for the determination of the carbon-14 activity.

Acetamidine. An aliquot of an aqueous solution of the irradiated sample, containing carrier acetamidine, was made strongly basic with a 16% sodium hydroxide solution and heated gently. After cooling, the solution was adjusted to a pH of 7.0 with dilute hydrochloric acid. To this was added a hot ethanol solution containing benzylthiuronium chloride. The precip-



itate was filtered, washed with water and recrystallized to a constant specific activity from dioxane.(37) A weighed portion of the derivative was dissolved in 95% ethanol and added directly to the scintillator solution.

Methylhydrazine. After adding carrier methylhydrazine, a 50% aqueous sulfuric acid solution was added to an aliquot of an aqueous solution of the sample at 0°C. The precipitate, formed upon the addition of 95% ethanol, was filtered and recrystallized from 80% ethanol to a constant specific activity. A weighed portion of the precipitate was dissolved in sodium hydroxide and added to the scintillator solution.

Acetonitrile. Methylamine and formaldehyde were removed from an aliquot of an aqueous solution of the sample, after carrier addition, by precipitation as described previously. The acetonitrile was removed by distillation using carrier techniques, and dissolved directly into the scintillator solution; the activity of the sample was then determined.

Polymeric Material. Upon dissolution of samples of the irradiated cyanoguanidine in distilled water, a brown material was found to remain undissolved. The brown solid was found to be only slightly soluble in water.

Ten milliliters of distilled water were added to a 0.3 gm sample of the irradiated cyanoguanidine and the solution centrifuged. The procedure was repeated with another distilled water wash and finally with acetone. The acetone was removed by air evaporation and the solid dried at 120°C for 30 minutes. The brown solid was dissolved in sodium hydroxide, added to the scintillator solution and counted. The brown polymeric material was found to contain about 13% of the total activity.

A portion of the brown material was mixed thoroughly with a small amount of mineral oil to form a mull and subjected to infrared analysis using a Perkin-Elmer Model 137 Infracord Spectrophotometer. An infrared analysis of authentic melamine in a similar mineral oil mull was also obtained. The infrared analysis of the brown material showed the same absorption bands, particularly the significant 12.25 millimicron band, as those obtained for the pure melamine, indicating that at least a portion of this polymeric material is melamine.

Pure melamine has been reported to show a sharp ultraviolet absorption band at 236 millimicrons(19). A small sample of the brown solid was dissolved in 0.1 N hydrochloric acid and the ultraviolet spectrum was made using a Cary Model 11 Recording Spectrophotometer. An ultraviolet spectrum was also obtained for a sample of authentic melamine in 0.1 N hydrochloric acid. The analysis of the pure melamine showed a reasonable sharp absorption at 236 millimicrons, followed immediately by a very broad, intense absorption band extending to about 200 millimicrons. The analysis of the brown material did not show a sharp absorption at 236 millimicrons; however the broad absorption band observed for the authentic melamine was observed in the analysis of the brown material. These results suggest that other materials are present in the brown solid in addition to melamine.

The solubility of pure melamine has been reported in The Merck Index(39) to be slightly soluble in water at 20°C. An approximate correction for the solubility of the brown material in water has been applied in reporting the total activity determined.



### Radiochemical Counting Techniques

Carbon-14 was the only radioactive element present in the irradiated cyanoguanidine. This eliminated any preferential determination of one isotope with regards to another isotope present in the sample and also eliminated any possibility of contamination in the separation of the various fractions by another isotope present in the sample.

Carbon-14 decays by negatron emission with a half-life of 5760 years(26). The low energy of the emitted beta particles influences the choice of techniques to be employed in counting the carbon-14 activity. The two principle methods employed in this study were ionization chamber counting of gaseous samples, and liquid scintillation counting of solutions. As was mentioned earlier, proportional counting was employed for a few radioanalysis made using gas chromatographic techniques.

Ionization chamber counting techniques using a vibrating reed electrometer were employed for gaseous samples. The gaseous sample to be counted was allowed to enter the evacuated ionization chamber and the chamber closed off by means of a valve. Inactive, anhydrous carbon dioxide was used to bring the pressure in the chamber to atmospheric pressure. The ionization chamber was placed on the vibrating reed electrometer head, allowed to reach equilibrium and the activity measured by the rate of drift method at 105 volts. This method of activity determination was not entirely satisfactory, however, due to the long periods of time required for the gaseous sample within the ionization chamber to reach equilibrium. In many cases, up to 72 hours was required before the system reached equilibrium. The necessity to convert all of the derivatives isolated in the analysis to carbon

dioxide and the inability to reproduce many of the results also contributed to the dissatisfaction with this method. Therefore, results obtained by these means were discarded, and emphasis placed upon liquid scintillation counting.

The liquid scintillation counting technique proved to be a very versatile and convenient method for the determination of the activity isolated in the analysis. Each derivative isolated was dissolved either directly or by use of a suitable solvent into the scintillator solution. The direct dissolution of the isolated material was preferred when feasible. All activity measurements were made using a Packard Tri-Carb Liquid Scintillation Spectrometer(31). The voltage on the two photomultiplier tubes had an average value of 840 volts. The attenuators were set at 1.0, which caused an amplification of the pulses received from the pre-amplifiers of about 3,000. With the low-level discriminator set at 10.0 and the high-level discriminator set at 50.0, the gate width was set on the maximum energy of the 0.155 Mev beta particle emitted from carbon-14. The scintillator solution used in this study consisted of a solution of 50.0 mgm of POPOP (1,4-bis-2-(5-phenyloxazole) benzene), 7.0 gm of PPO (3,5-diphenyloxazole) and 100 gm of naphthalene in one liter of p-dioxane. A counting efficiency of  $(50.0 \pm 1.4)\%$  was obtained using standardization samples of benzoic acid- $C^{14}$  obtained from three different sources(18, 32, 41). The error quoted above is one standard deviation.

Counting efficiency studies were performed on each derivative solute counted in these determinations. The effect of some typical added components on the counting efficiency of the scintillator solution described above is given in Figure 2. Figure 2 shows that both the addition of N,N'-methylphenylthiourea and concentrated ammonium hydroxide decrease the counting efficiency of the scintillator solution markedly. The addition of water to the scintillator

solution effects the counting efficiency of the scintillator solution to a much smaller extent. A plot of the theoretical count rate and the observed count rate as a function on concentration of N,N'-methylphenylthiourea is given in Figure 3. The broken line is the theoretical count rate based on the carbon-14 concentration and the solid line is the count rate experimentally observed. It has already been observed that the addition of the N,N'-methylphenylthiourea decreases the counting efficiency of the scintillator solution. A plot of  $\log (N/C)$  versus C, where N is the counts per minute and C is the concentration of the N,N'-methylphenylthiourea, is shown in Figure 4. The half-quenching concentration value of 28 mg obtained from this study is comparable to the value of 25 mg for a similar compound, p-tolylphenylthiourea(33).

The samples were prepared for counting by either dissolving the carrier derivative directly into the scintillator solution or by dissolution into a minimum amount of a suitable solvent. The counting vials consisted of a special glass, designed especially for liquid scintillation counting. After dissolution of the sample into the scintillator solution, the sample vials were cooled for 5-10 minutes prior to counting. The effect of the carrier derivative on the counting efficiency of the scintillator solution was determined for each carrier isolated. In this manner, corrections for the decrease in the counting efficiency of the scintillator solution were applied to the calculations of the specific activity of the particular carrier.

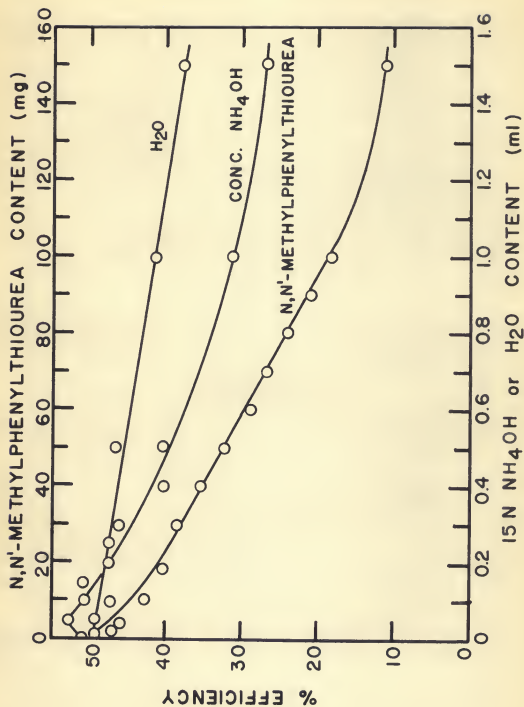


FIGURE 2 EFFECT OF SOME SOLUTES ON EFFICIENCY

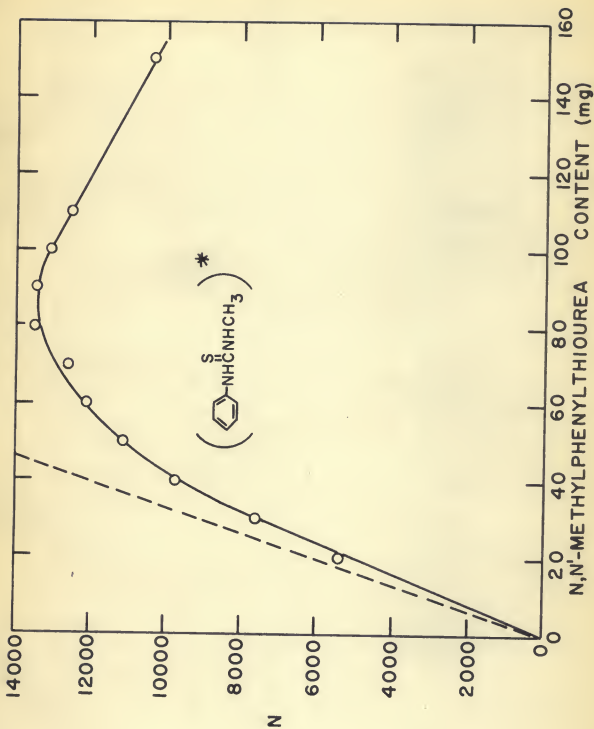


FIGURE 3 EFFECT OF N,N'-METHYLPHENYLTHIOUREA ON EFFICIENCY

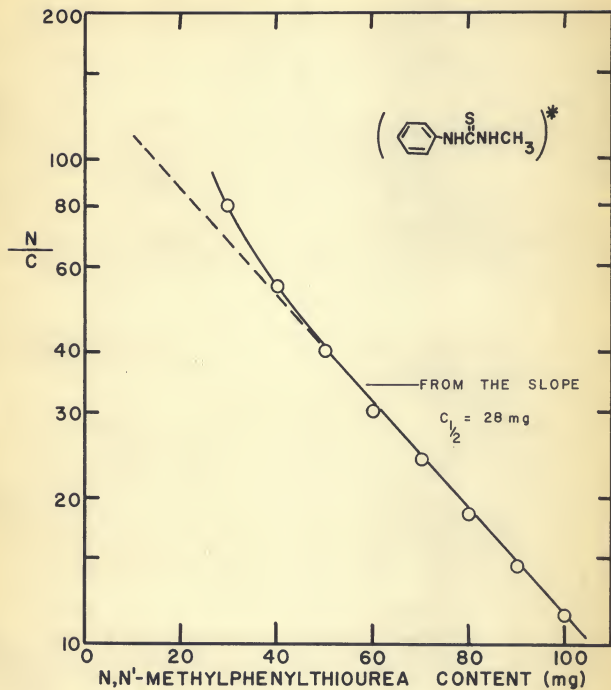


FIGURE 4 LOGARITHMIC PLOT OF FIGURE 3

## RESULTS AND DISCUSSION

One of the important results obtained in this study is the essentially complete determination of the carbon-14 containing compounds produced by the neutron irradiation of a complex organic compound in the crystalline state. Previous studies have shown that a complete determination of all the chemical species containing the recoil carbon-14 atom has been essentially limited to inorganic and simple organic compounds. Results have shown that in complex crystalline organic compounds, only 25-50 per cent of the total activity induced into the sample by the neutron irradiation is usually isolated in stable chemical species.

The total carbon-14 activity of the irradiated sample was determined by dissolution of a known portion of the solid in water. Aliquots were taken of the dissolved sample and the total activity determined by liquid scintillation counting. The average of four different determinations made over a period of four months was  $18.6 \pm 0.7$  microcuries for the 4.952 gm sample; i.e., a specific activity of  $3.76 \mu\text{C/gm}$ . The error quoted is one standard deviation. The total amount of carbon-14 activity expected for the sample was calculated to be 31.1 microcuries, based on the carbon-14 half-life of 5,760 years and an anticipated irradiation time of 672 hours. The pile neutron irradiation of the sample produced approximately 60 per cent of the calculated activity. This value is not unreasonable since the pile is shut down for loading and unloading operations four days of the month and since the exact neutron flux at the location of the sample position in the pile was not known.

The results obtained by the isolation procedures described in the



Experimental Section are given in Table 1. In all cases, the data reported are based on specific activity measurements. The percentage activity is based on the total activity of an aliquot of an aqueous solution of the original irradiated cyanoguanidine sample. The total activity isolated in this study was 90.1 per cent of the total carbon-14 activity induced in the cyanoguanidine sample by pile neutron irradiation.

In this investigation we have considered only the final chemical form incorporating the recoil carbon-14 atom. It has been previously suggested(56) that many chemical forms of the recoil carbon-14 atom are present within the solid matrix following irradiation. Many of these matrix-stabilized chemical forms undergo decomposition, rearrangement or further reactions when the solid irradiated compound is dissolved in water to give chemically stable species which may be isolated from an aqueous solution of the irradiated compound. Since only the final form assumed by the recoil carbon-14 is actually determined, these matrix-stabilized species can be arrived at only by a critical analysis of the results obtained from a particular determination and the proposition of reasonable intermediates to yield the products actually observed. From the consideration of a number of studies, a similarity in the final form of the recoil atom may become evident. Considerations of the similarities can lead to a better characterization of the matrix-stabilized species resulting from the irradiation.

The final state of the carbon-14 recoil atom may be considered in terms of three steps, any one of which may have an effect upon the final distribution of activity.(50) The first steps involves the reduction of the energy of the recoil atom by elastic and inelastic collisions and the final localisation



Table 1. Carbon-14 Distribution Among Various Compounds

<u>Fraction</u>	<u>Per cent of Total Activity</u>	
	<u>Average</u>	<u>Values Obtained</u>
$\text{CH}_4$	0.0	0.0, 0.0
CO	0.0	0.0, 0.0
$\text{CO}_2$	0.0	0.0, 0.0
HCN	0.0	0.0, 0.0
HCHO	0.1	0.2, 0.1, 0.1
HCOOH	0.4	0.5, 0.4, 0.4
$\text{CH}_3\text{CN}$	0.6	0.9, 0.3
$\text{CH}_3\text{NH}_2$	3.2	3.3, 3.1
$\text{CH}_3\text{NHNH}_2$	1.0	1.3, 0.7
$(\text{NH}_2)_2\text{CO}$	0.2	0.4, 0.2, 0.1
$(\text{NH}_2)_2\text{C=NH}$	13.5	14.3, 14.1, 13.9, 12.9, 12.4
$\text{CH}_3\text{C}(\text{NH})\text{NH}_2$	16.9	17.7, 17.0, 16.6, 16.2
$\text{NCNC}(\text{NH})\text{NH}_2$	41.1	42.6, 39.6
Melamine	13.1	13.5, 12.7

of the recoil atom in a reactive site. The second step involves the chemical considerations which may lead to a variety of solid matrix-stabilized chemical species depending upon the structural aspects of the entrapment site and upon the energy available for chemical reactions within the reactive site. The third step considers the collapse of the solid matrix-stabilized species to form stable compounds or the reaction of the stabilized species during subsequent chemical operations carried out on the irradiated material to form stable chemical species. Each of the foregoing steps, however, involves several factors.

Factors to be considered in the first step are: (1) the energy of the recoil atom or fragment previous to the final localization in a reactive site, (2) the structural aspects of the recoiling atom or fragment during the period before the final localization, and (3) the probability of interaction of the recoil atom or fragment with a particular bond, molecule or atom. The factors involved in the second step include: (1) the probability of the formation of a number of chemical species which will lead to the formation of stable products, (2) the effect of the surroundings on the final distribution of the recoil atom among the various products. The third step involves: (1) the probability that an intermediate will collapse to give a stable compound, and (2) the consideration of whether or not a compound can be isolated by the chemical procedures employed and the influence of the separation procedures on the activity distribution.

#### Distribution of Carbon-14 Recoil Atom

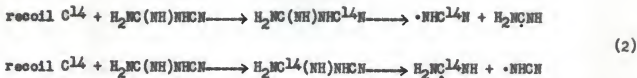
The absence of activity in the oxygen-containing gases evolved from the sample upon dissolution in water would be expected since oxygen was not

originally present within the molecule. This absence supports the results obtained by Yankwich(56, 59) for ammonium bromide and ammonium sulfate. In the oxygen-containing compound, 42 per cent of the activity was present as carbon dioxide and carbon monoxide while in the ammonium bromide only 3 per cent of the total activity was present in carbon dioxide and carbon monoxide. The relatively small amounts of activity present in the "simpler" compounds, such as formaldehyde, hydrogen cyanide and formic acid, indicates the formation of skeletons of complex chemical species and that these species persist in the irradiated crystals. Formation of the "simpler" compounds would occur by the presence of a matrix-stabilized intermediate species such as  $\text{CH}_2=\text{NH}$ , which when dissolved in water would undergo hydrolysis to form formaldehyde. The results indicate that the fragmentation of the surrounding molecules by the recoil carbon-14 atom does not produce a complete dissociation of the molecules, but rather leads to the formation of two or three larger fragments of the parent molecule. This could explain the absence of activity in the "simpler" compounds.

An important result of this study is that nearly one-half of the total activity produced in the pile-neutron irradiation was found in the parent compound, cyanoguanidine. This differs significantly from results previously reported(47) in which only a small fraction of the total activity has been "retained" in the parent compound. The formation of the cyanoguanidine may be postulated to occur by equations (1) and (2).



and

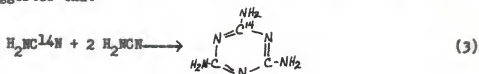


The carbon-14-containing cyanamide radicals, resulting from the fragmentation of the parent compound, might subsequently dimerise, either with each other or with other inactive cyanamide radicals produced by the fragmentation of the cyanoguanidine molecule to reform the parent compound. This possibility becomes more plausible in light of the results obtained by Ma(25) in the thermal decomposition studies of guanidine chromate and guanidine dichromate. Ma found(25) that at elevated temperatures cyanamide was produced and the major share of the cyanamide dimerized to form cyanoguanidine. By considering the temperature attained in the local hot-spot regions according to the Seitz-Koehler(36) description of the displacement of atoms, it appears reasonable that the high "retention" of the induced carbon-14 activity in the parent compound occurs by the formation of cyanamide, which dimerizes within the local hot-spot region to form cyanoguanidine.

The formation of the two cyanamide radicals resulting from a "knock-on" reaction with the recoiling carbon-14 atom may be rationalised by consideration of the nature of the groups attached to the central carbon atom and the adjacent nitrogen atom. In organic chemistry, the  $C\equiv N$  group is considered a moderately strong electron attracting group. The  $C\equiv N$  group may attract electrons and consequently tend to weaken the bonding between the nitrogen and carbon in the single bond. The nitrogen atom would now be somewhat deficient of electrons and, being more electronegative than carbon, would tend to attract the electrons from the single bond between itself and the central carbon atom. The attraction of these electrons would weaken the

single bond between the nitrogen and the central carbon atom. The imine group, bonded to the central carbon atom, is also an electron-attracting group, although not as strong as the  $C\equiv N$  group. Attraction of electrons by this group would also weaken the single bond between the central carbon atom and the nitrogen atom. From this consideration of the nature of the groups present in the cyanoguanidine molecule, one could reason that the single bond between the central carbon atom and the nitrogen atom is perhaps the weakest bond within the molecule. This bond would most likely be broken by the "knock-on" reaction with the recoiling carbon-14 atom.

At least a portion of the polymeric material observed in this study has been tentatively identified as melamine. Infrared and ultraviolet spectrophotometric results have shown that a component of the polymeric material is melamine. The possibility of other chemical species, in much smaller amounts, cannot be disregarded, however. In view of the actual amount of the material isolated, a complete analysis of all components present in the polymeric solid would be extremely difficult. It is speculated that the formation of melamine occurs in much the same manner as the formation of cyanoguanidine. The formation would involve a trimerisation of the cyanamide radicals produced within the local hot-spot regions. This speculation is supported by Glasner and Makovsky's(12) studies of the thermal decomposition of guanidine perchlorate in which they report that guanidine perchlorate dissociates in the region of 300-450°C to give considerable amounts of cyanamide, which trimerises at elevated temperatures to form melamine. It is suggested that



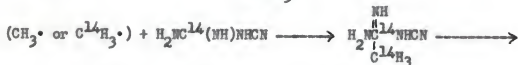
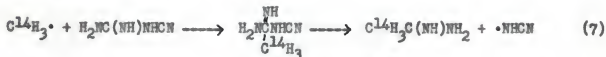
The results of this study have shown that, in addition to the parent compound and the polymeric material, a significant amount of activity (> 10%) was found in only two other compounds, guanidine and acetamidine. A possible mechanism for the formation of guanidine is



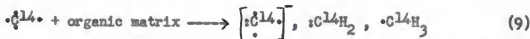
and for the formation of acetamidine, possible mechanisms are



Alternate possibilities for the formation of acetamidine-C<sup>14</sup> could be through the "knock-on" reactions,



The recoiling carbon-14 is a very reactive radical and when its motion becomes essentially diffuse, the carbon-14 can react with its surroundings to produce a variety of molecular species(50).



The carbon-14 containing methyl radical may then undergo the reactions postulated in equations 5-8. The carbon-14 containing compounds obtained through such a mechanism would contain C<sup>14</sup> atoms either in the methyl group

or at both carbon positions. The production of acetamidine with the carbon-14 only in the central carbon position would require the formation of an unlabeled methyl radical, since a methyl group, as such, does not exist in the cyanoguanidine molecule. The formation of this methyl radical may be postulated in much the same manner as that suggested by equation 8. The carbon radical could conceivably be formed as a result of fragmentation due to the recoiling C<sup>14</sup> atom through the organic matrix.

Cyanoguanidines, containing the carbon-14 atom at either carbon position would require the dimerisation of a labeled cyanamide radical with an unlabeled cyanamide radical produced within the same hot-spot. The formation of doubly-labeled cyanoguanidine, however, would require the dimerisation of two labeled cyanamide radicals. This would necessitate the diffusion of one of the labeled radicals through the crystalline organic matrix to another hot-spot produced by a recoiling carbon-14 atom. Another possibility could be that in the combination of the various hot-spots to form a hot zone or "displacement spike", two labeled cyanamide radicals may occur within a proximity sufficiently close to allow the dimerisation of the two radicals to form the doubly-labeled cyanoguanidine molecule. One could reasonably assume the probability of two labeled cyanamide radicals dimerising to form the doubly labeled parent compound is low and that the cyanoguanidine molecule is labeled in either of the carbon positions but only to a smaller extent in both positions. In the formation of melamine, essentially the same mechanism may be postulated as for the formation of cyanoguanidine. The most probable species resulting from the trimerisation of three cyanamide radicals to form the melamine molecule would be one which contains a carbon-14 atom at only one of the carbon positions. The probability for the formation of a triply



labeled molecule, necessitating the trimerization of three labeled cyanamide radicals, would likely be very low. The probability for the formation of a doubly labeled species would also be expected to be small.

#### Radiocarbon Product Distribution

Yankovich(55) has stated that chemical consequences of the two different final environmental situations, predicted from the Libby(20, 21) and Seitz-Koehler(36) models, would be quite similar for simple ionic crystals. A different chemical phenomena would occur for molecular crystals or ionic solids containing molecular ions. Production of a long-lived, high temperature hot-spot, predicted by the Libby model, would probably involve the complete dissociation of the molecule or molecular ion in the vicinity of the hot atom. As cooling occurred, competitive reactions among the various atoms would determine the nature of the chemical species observed upon dissolution of the target in a solvent. Where a short-lived, lower temperature hot-spot is produced, as predicted by the Seitz-Koehler model, only partial fragmentation of the molecule or molecular ion would likely result. Upon cooling, competitive reactions among various atoms and fragments would determine the distribution of radiocarbon in the various chemical species upon dissolution in a suitable solvent. The Libby model predicts a concentration of energy sufficient to permit the formation of species capable of oxidizing the recoil carbon-14 atom; the Seitz-Koehler model predicts that much less energy will be available within the hot-spot and that species capable of oxidizing the recoil atom would not be formed.

In simple ionic crystals where a few carbon-containing species can be formed and where only one or two types of hot-spot environment can occur,

the amount of energy available in the terminal hot-spot may exert a strong influence on the final chemical state of the recoil atom. The distribution of product radiocarbon among the various oxidation states may be a reflection of the distribution of energy in the terminal hot-spots. Libby's model predicts a dependence of the final chemical state upon the recoil energy of the atom. In the Seitz-Koehler model, no processes have any chemical consequences prior to the entrapment of the recoil atom so that the variation of recoil energies has no effect upon the final chemical state of the recoil atoms, provided the recoil energy is greater than the entrapment energy.

If the charges on the ions in a simple ionic crystal are similar, one would expect the carbon-14 recoil atom to exhibit a symmetrical distribution of oxidizing and reducing character resulting in a symmetrical distribution of the radiocarbon among the various oxidation states, providing the reactions of the entrapped radicals are not entirely of one nature.

The distribution of the recoil carbon-14 atom among the various oxidation states for several compounds is shown in Table 2. In the foregoing discussion, it was stated that simple ionic crystals should show a symmetrical distribution of the radiocarbon among the various oxidation states, while the distribution for molecules or ionic solids containing molecular ions depends upon the competitive reactions occurring within the hot-spot. The distribution of the radiocarbon among the various products in the beryllium nitride study confirms the expectation of a symmetrical distribution of the recoil atom among the various oxidation states in a simple ionic crystal. If one compares the total activity occurring in the negative oxidation states with that occurring in the positive oxidation states, an essentially equal

Table 2. Distribution of Carbon-14 Among Various Final Products of the (n,p) Reaction on Nitrogen-Containing Compounds

Oxidn. No.	Final Product	$\text{H}_2\text{NC(NH)NHCN}$	$\text{NH}_4\text{Br}$	$(\text{NH}_4)_2\text{SO}_4$	$(\text{NH}_4)_2\text{C}_2\text{O}_4$	$\text{Be}_3\text{N}_2$
Ref.		*	59	56	11	57
-4	$\text{CH}_4$	0.0	7.5	0.5		25.8
-2	$\text{CH}_3\text{NH}_2$	3.2	79.1	16.1		4.1
	$\text{CH}_3\text{NHNH}_2$	1.0				11.2
0	$\text{HCHO}$	0.1	5.8	13.2		2.4
+2	$\text{CO}$	0.0	1.3	2.0	4.8	0.1
	$\text{HCOOH}$	0.4	1.3	15.5		8.3
	$\text{HCN}$	0.0	2.0	3.9	1.5	6.5
	$\text{CH}_3\text{CN}$	0.6				
+3	$(\text{COOH})_2$				11.3	
+4	$\text{CH}_3\text{C(NH)NH}_2$	16.9				
	$\text{CO}_2$	0.0	1.7	39.5	5.8	14.4
	$\text{CO(NH}_2)_2$	0.2	0.4	7.3		6.2
	$\text{CNH(NH}_2)_2$	13.5	0.0	0.0		18.7
	$\text{H}_2\text{NC(NH)NHCN}$	41.1				
	Melamine	13.1				

\* Results of this study

distribution is found. The unsymmetrical radiocarbon distribution among molecules and ionic crystals containing molecular ions is clearly demonstrated by the remaining compounds in Table 2. The ammonium bromide, sulfate and oxalate are ionic crystals containing a molecular ion, the ammonium ion, while cyanoguanidine is a molecular crystal. The results obtained in the ammonium bromide study show approximately 90 per cent of the activity present in the negative oxidation states with almost 80 per cent of the activity present in the negative two oxidation state. In sharp contrast, ammonium sulfate and cyanoguanidine have shown 68 and 86 per cent, respectively, of the total activity present in the positive oxidation states, with 85 per cent of the total activity of cyanoguanidine and 47 per cent of the activity of ammonium sulfate occurring in the positive four oxidation state. The results obtained for ammonium oxalate are incomplete, with only 24 per cent of the total activity determined. The results, however, show all the activity observed is present in the positive oxidation states.

The results of the present study on the neutron irradiation of crystalline cyanoguanidine agree very well with the results previously reported for other systems irradiated in the crystalline state in showing the unsymmetrical distribution of the recoil carbon-14 atom among the various oxidation states of the radiocarbon products resulting from molecules and ionic solids containing molecular ions.

## SUMMARY

Activity measurements were made using liquid scintillation counting techniques. A counting efficiency of  $(50.0 \pm 1.4)$  per cent was obtained using a scintillator solution consisting of POPOP, PPO and naphthalene in *p*-dioxane. The effect on the counting efficiency of the addition of various solutes to the scintillator solution was also studied.

The neutron irradiation of crystalline cyanoguanidine produced the incorporation of the recoil carbon-14 atom in several stable chemical species. The parent compound, cyanoguanidine, was observed to contain approximately 40 per cent of the total activity produced by the neutron irradiation. Guanidine, acetamidine, and a polymeric material, believe to be melamine, were found to contain 17, 13.5, and 13 per cent, respectively, of the total activity induced in the sample. Small amounts of activity were found in the form of formaldehyde, formic acid, methylamine and acetonitrile.

Reaction mechanisms, leading to the final incorporation of the carbon-14 recoil atom in the chemical species isolated, were postulated. The cyanamide radical, produced by the fragmentation of the cyanoguanidine, was suggested to be the principle intermediate in the formation of cyanoguanidine, melamine, guanidine, and acetamidine.

Radiation damage, due to the gamma-ray flux accompanying the thermal neutrons in the pile irradiation, was calculated to have damaged about 12 per cent of the sample.

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CARBON-14-CONTAINING COMPOUNDS PRODUCED BY  
THE FINE-NEUTRON IRRADIATION OF CYANOGLUANIDINE

by

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The chemical effects produced by the  $N^{14}(n,p)C^{14}$  nuclear reaction on crystalline cyanoguanidine were studied after the pile-neutron irradiation by dissolving the sample in water and investigating the nature and relative amounts of the radiocarbon-labeled products.

Radioactivity measurements were conveniently made using liquid scintillation counting techniques. A counting efficiency of  $(50.0 \pm 1.4)$  per cent was observed using a scintillator solution of POFOP, PFO and naphthalene in p-dioxane. The effect of various solutes on the counting efficiency of the scintillator solution was studied. N,N'-methylphenylthiourea and concentrated ammonium hydroxide were found to produce a marked decrease in the counting efficiency, while the addition of water had little effect on the counting efficiency.

The investigation of the nature and relative amounts of the radiocarbon-labeled products showed that little activity was present in the form of CO, CO<sub>2</sub>, CH<sub>4</sub>, HCN, CH<sub>3</sub>CN, HCHO, HCOOH, urea and methylhydrazine. Acetamidine, guanidine, and a polymeric material, believed to be melamine, were found to contain 17, 13.5 and 13 per cent, respectively, of the total induced activity. The parent compound, cyanoguanidine, was found to contain 41 per cent of the total activity induced in the sample by the neutron irradiation.

Possible mechanisms for the formation of cyanoguanidine, acetamidine, guanidine and melamine are suggested. Cyanamide, produced by the fragmentation of the cyanoguanidine molecule, is considered to play an important role in the formation of the final products observed in solution. Interpretation of the observed results is made in terms of the Seitz-KoeHLer

"displacement spike" model of the effects of irradiation on crystalline materials.

The results observed in this study are compared to previously reported results for the neutron irradiation of nitrogen-containing organic and inorganic compounds in the solid state.